

**Polyolefin Production using Condensing Mode in Fluidized Beds, with Liquid
Phase Enrichment and Bed Injection**

Related Application

5

This is a continuation-in-part of US Patent Application Serial Number 09/514,440 filed 2/28/00 by the same inventors and having the same title.

Technical Field of the Invention

10

This invention relates to gas phase exothermic reactions to make particulate product in fluidized bed reactors. The invention is described with respect to olefin polymerization but is not limited to the production of polymeric products; rather, it may be practiced in connection with any exothermic reaction which is carried out in a gas fluidized bed with external cooling. It relates particularly to improvements in the condensing mode of operation in which a portion of the fluidizing gas or fluid is withdrawn from the reactor, cooled to remove the heat of reaction, partially condensed, and recycled back to the fluidized bed reactor. In the present invention, the recycle is effected by splitting the recycle stream in at least two streams directed to different areas of the reactor.

Background of the Invention

The gas phase fluidized bed process for polymerization permits a reduction in energy requirements and capital investment compared with more conventional processes. However, a limiting factor is the rate at which heat can be removed from an exothermic reaction occurring within a fluidized bed. The heat of reaction is commonly removed from the fluidized bed by compression and cooling of a recycle stream external to the reactor vessel. The circulated recycle stream promotes fluidization of the bed within the reactor. The fluid velocity within the

-2-

reactor is limited by the need to prevent excessive entrainment of solids in the fluidizing gas stream as it exits for recycle from the reactor. Hence the amount of fluid which can be circulated and cooled per unit of time to remove the exothermic heat of polymerization is limited. As polymer product is produced and removed from the fluidized bed, reactants and catalyst material are continuously supplied either to the recycle stream or directly to the reaction zone of the fluidized bed.

The quantity of polymer exothermically produced in a given volume of the fluidized bed is related to the ability to remove heat from the reaction zone. Adequate heat removal is critical to maintain a uniform temperature within the fluidized bed and also to avoid catalyst degradation and polymer agglomeration. The temperature in the reaction zone is controlled below the fusing temperature of the polymer particles. The dew point of the recycle stream is the temperature at which liquid condensate begins to form in the recycle stream. By cooling the recycle stream below the dew point temperature and then injecting the two phase mixture thus formed into the reaction zone, the heat of vaporization of liquid is available to consume a portion of the exothermic heat of polymerization. This process is known as "condensed mode" operation of a gas phase polymerization process. As disclosed by J. M. Jenkins et al. in U. S. Patents Nos. 4,543,399 and 4,588,790 and by M. L. DeChellis, et al. in U. S. Patent 5,352,749, operation in "condensed mode" permits an increase in the space time yield of the reaction system – that is, an increase in the amount of polymer produced per unit of time in a given fluidized bed reactor volume.

25

Below the reaction zone of the fluidized bed is a gas distributor grid plate. Its function is to provide a uniform distribution of the recycle stream into the bottom of the bed. Below the gas distributor grid plate is located a bottom head mixing chamber where the recycle stream is returned after being compressed and cooled. As disclosed by S. J. Rhee, et al., in U. S. Patent 4,933,149, flow deflection

30

-3-

devices can be designed and positioned within the bottom head mixing chamber, to avoid excessive build up of entrained solids within the bottom head mixing chamber when operating without partial condensation of the recycle stream. When operating in “condensed mode”, a deflector geometry as disclosed in the

5 ‘149 patent may be used to avoid excessive liquid flooding or frothing in the bottom head mixing chamber. However, as the condensing level is increased to further enhance heat removal and space time yield, excessive amounts of liquid can exist in the bottom head mixing chamber. This can lead to liquid pooling and instability problems.

10

The fluidized bed discharge process described by Aronson in U. S. Patent 4,621,952 is an intermittent semi-batch process involving the transfer, by pressure differential, of solid and gas through multiple vessels. Being semi-batch in nature, the product removal capacity of a given facility is constrained by the time duration

15 of the steps necessary to complete the process. The Aronson discharge process includes interconnecting conduits with valves between the vessels to permit gas venting and pressure equalization. The gas contains valuable raw materials for the fluidized bed reaction system. The gas may include unreacted monomers and comonomers; inert materials are also common. Aronson discloses that the

20 discharge process obtains the desired transfer of solid material while minimizing gas losses. Aronson does not, however, monitor liquid in the product discharge tanks or inject fluid to a point higher than product withdrawal.

As disclosed by Jenkins, et al., in U. S. Patent 4,543,399 and by Aronson in U. S.

25 Patent 4,621,952 the polymer product is intermittently withdrawn from the fluidized bed at an elevation above the gas distributor grid plate. At increasing levels of partial condensation of the recycle stream the likelihood increases that undesirably high levels of liquid phase may exist in lower portions of the fluidized bed. Unfortunately during a product discharge event liquid can be carried out of

30 the reactor along with the granular polymer and gases. Because of the

-4-

- depressurization which takes place during product discharge, the liquid expands and vaporizes, which may cause temperature reduction and pressure elevation within the discharge equipment. This can reduce the fill efficiency of the discharge system, and the reduction in fill efficiency in turn reduces the production capacity by increasing the time to depressurize, and increases the raw material usage of the process. Accordingly, it has been difficult to increase the liquid content in the recycle stream to enhance the efficiency of removing the heat of reaction.
- 10 In Chinh et al, in US Patent 5,804,677, the patentees assert they describe the separation of liquid from a recycle stream; the separated, collected liquid is injected into the fluidized bed above the gas distributor plate. The present invention also injects recycle liquid above the distribution plate, but applicants' liquid is handled as a liquid/gas mixture and as a more or less predetermined
- 15 fraction of the recycle stream, as a slip stream, divided simply and directly in the recycle conduit. Because of the applicants' manner of separating, we are able to enhance the ratio of liquid to gas in the slip stream as compared to the withdrawn recycle stream, and thus simply and directly, without additional or special equipment, improve heat exchange efficiency and enhance the space/time yield of
- 20 the process. In addition, we are able to optimize the product discharge cycle by coordinating liquid volume in the discharge tanks with the rate of injection of liquid above the distributor plate.

Summary of the Invention

25

Our invention comprises splitting the recycle stream, after compression and cooling, into at least two streams. One of the streams is returned to the distributor grid plate or similar device below or near the bottom of the bed and the other(s) are returned to the fluidized bed at one or more points above the

-5-

distribution grid plate. The stream is split by a conduit segment designed for the purpose, sometimes herein called a splitter.

Preferably, the recycle stream is divided into two streams, the smaller of which is 5 to 30 percent of the total recycle stream and contains an enrichment of the liquid portion as a function of the relative momentums of the liquid and gas components of the recycle stream, impacting in the splitter, the liquid droplet size, and the particular configuration of the splitter. The liquid content (percentage by weight) of the smaller stream is preferably enriched to a percentage 1.01 to 3.0 times, more preferably 1.1 to 2.5 times that in the stream prior to separation. The larger of the separated streams, having a lower liquid concentration but a higher volume, is recycled to the bottom head mixing chamber of the reactor vessel and introduced into the reaction zone in a uniform fashion more or less conventionally through a gas distributor grid plate. The smaller stream or streams having an enriched liquid phase, is (or are) recycled into the reaction zone at an elevation above the gas distributor plate. Because of the lower ratio of liquid to gas in the larger stream as compared to the original cooled/condensed stream, only a minimal disturbance of the fluidized bed is imparted. We are thus able to inject higher quantities of recycled liquid into the bed without causing difficulties in the product withdrawal system.

An attractive novel feature of our modified recycle technique is that the separation of the recycle stream may be conducted without using mechanical equipment such as separators, hydrocyclones, demisters, scrubbers, entrainment collection devices, pumps, compressors or atomizers. Rather, by withdrawing the small two phase stream or streams from the recycle piping line, by the use of an elbow, bend, tee, or other piping configuration, an enrichment occurs of the liquid content in the small stream. This occurs without any moving parts or the application of energy. This enrichment is due to the difference in momentum between the lower density vapor phase and the higher density liquid phase. As a result of inertia, the liquid

-6-

droplet trajectories deviate from the streamline of the bulk vapor flow. The liquid phase may exist in the form of droplets ranging in size from 50 to 2000 microns. By selection of a suitable piping system, the small stream or streams, which have been enriched in liquid content, may be re-injected into the reaction zone of the fluidized bed at a location above the gas distributor grid plate, preferably above the product withdrawal level. In this manner a large quantity of the condensed liquid exiting the cooler can be injected into the upper portions of the fluidized bed without separating the gas and liquid phases using mechanical equipment. This is an advantage over the methods disclosed by Chinh, et al. in U. S. Patents Nos. 5,541,270, 5,668,228, 5,733,510 and 5,804,677 (see the summary above) in that the financial costs for mechanical equipment such as separators, hydrocyclones, demisters, scrubbers, entrainment collection devices, pumps, compressors or atomizers are not incurred. Some of these have moving parts and all entail substantial maintenance problems. The advantage compared to conventional technology incorporated by Union Carbide Corporation and disclosed by Jenkins, et al. in the U. S. Patents Nos. US 4,543,399 and US 4,588,790 is that the liquid re-injection into the reaction zone of the fluidized bed can occur at one or more points above the gas distributor grid plate without substantial disturbance of the fluidized bed.

20

We use the term "splitter" to mean an elbow, bend, tee, or other conduit segment having an inlet (upstream) portion and two or more outlet (downstream) portions. The outlet portions may be configured, either by a reduction in overall internal diameter or by one or more obstructions or diversions, to provide a resistance to the flow of fluid, which will, to at least some degree, cause liquid to coalesce or accumulate in at least one of the exit portions. Preferably, the incoming fluid is divided into a primary stream containing a high ratio of gas to liquid compared to the secondary stream(s) and at least one secondary or slip stream containing a relatively high ratio of liquid to gas compared to the fluid entering the splitter. The secondary stream may be larger – that is, the pipe diameter for the secondary

30

-7-

stream may be greater than that of the primary stream, and/or the flow of total fluid may be greater in the secondary stream, but we prefer that the secondary stream – the stream containing a higher ratio of liquid to gas – be of a smaller diameter than the primary stream. We use the terms “secondary stream,” “bypass,” and “slip stream” interchangeably. There may be more than one secondary or slip stream. Further, the primary stream may be directed to another splitter to be further split into additional streams, at least one having an enhanced ratio of liquid to gas compared to the fluid entering it, for additional injection into elevated regions of the reactor, preferably above the product withdrawal level. However, fluidization of the bed **2** (**Figure 1**) must be maintained throughout; fluidization requires a sufficient quantity and velocity of fluid through line **3** to distribution plate **7**.

We use the term “through a direct passage” to mean that the slip stream is passed directly from the elbow, bend, tee, or other conduit segment (splitter) to the reaction zone of the reactor, or to the upstream end of another splitter, without going through any mechanical equipment such as separators, hydrocyclones, demisters, scrubbers, entrainment collection devices, pumps, compressors or atomizers.

The ability to pass the slip stream through a direct passage into the reaction zone of the fluidized bed is enhanced by the usual slight reduction in pressure in the fluidized bed from its lower region to its upper region. Commonly, the pressure in the upper regions is from 0.04 to 0.15 psi per foot of height less than that in the lower regions of the bed. Thus, the higher the injection point in the bed, the greater will be the difference between the pressure in the slip stream and that in the reactor bed, which of course assists the flow of the secondary stream into the fluidized bed. Generally, we will inject the secondary stream at one or more points between six inches and 10 feet above the distributor plate of a commercial polyolefin reactor such as that shown in **Figure 1**, but we prefer to inject the

-8-

secondary stream at a height between eighteen (18) inches and ninety-six (96) inches above the distributor plate. Recycle injection is preferably above the point of product withdrawal.

- 5 Our invention includes a conduit segment which will provide a slip stream through a direct passage from a preferred elbow configuration defining a settling chamber and a discharge duct for the slip stream located at the bend of the elbow. More particularly, our invention includes a splitter for splitting a partially condensed recycle stream from a recycle stream in a fluidized bed polyolefin
- 10 reactor, the splitter comprising an inlet portion, a primary outlet portion communicating with the curved portion, a secondary outlet portion, the secondary outlet portion preferably including a settling chamber located downstream from, adjacent to, and on the outside radius of said curved portion, and a slip stream conduit communicating with the settling chamber, the slip stream conduit
- 15 preferably having a smaller effective diameter than that of the primary outlet portion and of the settling chamber.

- This invention is an improvement in the "condensed mode" of operation. As disclosed by Jenkins, et al. in U. S. Patents Nos. 4,543,399 and 4,588,790 and by
- 20 DeChellis, et al. in U. S. Patent 5,352,749, operation in "condensed mode" permits an increase in the space time yield of the reaction system – that is, the amount of polymer produced per unit of time in a given fluidized bed reactor volume. Also disclosed by DeChellis in the aforementioned U. S. Patent is that
- 25 excessively high levels of liquid introduced to the fluidized bed may promote the formation of undesirable polymer agglomerates, the presence of which can lead to bed collapse and reactor shutdown. Excessive liquids can also influence local bed temperatures which yield undesirable inconsistencies in polymer product properties.

-9-

Our invention provides an increase in the space time yield (polymer production per unit of time) of a reaction system of a given volume, compared to other condensed mode techniques. In particular, the separation of the partially condensed recycle stream is accomplished without the use of costly mechanical separating devices such as separators, hydrocyclones, demisters, scrubbers, entrainment collection devices, pumps, compressors or atomizers.

An important aspect of our invention is that the injection of liquid above the point of product withdrawal reduces the quantity of liquid carried out of the fluidized bed with the solid and gas during the discharge process. This improves the product removal capacity and the raw material efficiency of the semi-batch discharge process. Regulation of the liquid split as a function of monitored or modeled liquid in the discharge tanks enhances the efficiency of the system.

Brief Description of the Drawings

Figure 1 is a schematic illustration of the gas phase fluidized bed exothermic polymerization process, including the recycle stream separation and liquid enrichment system.

Figure 2 depicts an elbow installed at the desired separation point for the recycle stream to provide a slip stream for insertion to the reaction zone of a fluidized bed such as in **Figure 1**.

Figure 3 is a further illustration of a preferred splitter to emphasize its optional settling zone.

Figures 4, 6, 7, and 8 are velocity profiles with accompanying droplet distribution data within the preferred elbow configuration, as predicted by a computer simulation for various conditions and products.

Figure 5 is an 8-droplet projectory profile in a preferred elbow configuration.

Figures 9, 10, 11 and 11a show variations in elbows which may be used in our
5 invention.

Figure 12 is a schematic illustration similar to **Figure 1**, including multiple discharge tanks in parallel, similar to apparatus described by Aronson in U. S. Patent 4,621,952. The use of this apparatus in our invention is described in
10 Examples 17, 18, 19 and elsewhere herein.

Figure 13 illustrates a typical pressure equalization between vessels **10** and **10'**.

Detailed Description of the Invention

15

Referring to **Figure 1** of the drawings, a preferred embodiment of the system for carrying out the process of the invention is shown. The reaction vessel **1** contains a fluidized bed **2** of particulate product with a fluid recycle stream entering the bottom inlet line **3** and exiting through line **4** from expanded section **28**. Reaction
20 catalyst is supplied intermittently or continuously from a reservoir **5** to a point **6** above the gas distributor grid plate **7** immediately below the fluidized bed **2**. Polymer product is withdrawn intermittently or continuously through the discharge line **8** through valve **9** into tank **10**. The discharge tank **10** may be connected by valve **11** in series with another tank **12**. The polymer product is
25 subsequently transferred to downstream processing equipment through valve **13** and line **14** with the optional addition of transfer assist gas through line **15**. There are other ways known in the art to accomplish this product removal process and some are disclosed by Aronson in U. S. Patent 4,621,952. The invention is not limited to the production of polymer products, but rather may be practiced in
30 connection with any exothermic reaction which is carried out in a gas fluidized

-11-

bed with external cooling. Variations are well known in the art for maintaining the bed in a fluidized state, feeding the catalyst, feeding the monomer(s), and recovering unreacted monomer from the product stream. Our invention can readily accommodate such variations as applied by persons skilled in the art.

5

The recycle stream exiting through line 4 of our preferred system is passed through a compressor 16 and cooler 17. As the reaction proceeds raw materials such as monomers are introduced possibly to the recycle stream 3 through line 18 or at other locations of the process such as directly into the fluidized bed 2 or into
10 the recycle line 4. The maximum velocity of the recycle stream exiting through line 4 is constrained to avoid excessive entrainment of polymer particles into the recycle line. This is because the particles may tend to plug and foul compressor 16, cooler 17 and gas distributor grid plate 7. The function of the gas distributor grid plate is to provide a uniform distribution of the recycle stream into the bottom
15 of the bed. The reaction vessel 1 normally includes an expanded upper section 28 to permit a local decrease in the gas velocity and reduce the propensity for the removal of polymer particles from the reactor through the top line 4. The minimum velocity of the recycle stream in line 4 is normally several times the minimum needed to suspend the particles within the bed 2 in a fluidized state.

20

The cooler 17 removes the exothermic heat of polymerization and the heat of compression. Adequate heat removal is important to maintain a uniform temperature within the fluidized bed and also to avoid catalyst degradation and polymer agglomeration. The temperature in the reaction zone is controlled below
25 the fusing temperature of the polymer particles. Under steady state conditions, the temperature of the bed is nearly uniform. A temperature gradient exists within a small section of the bottom layer of the bed. Typically (and particularly in the absence of liquid introduction to the higher regions of the bed, as in the present invention) the temperature gradient does not extend above the first 12 inches of
30 the bottom of the bed 2. The temperature gradient is caused by the lower

-12-

temperature of the recycle stream which is returned to the bottom of the fluidized bed 2. As disclosed by Jenkins et al. in U. S. Patents 4,543,399 and 4,588,790, the discharge temperature of the recycle stream exiting the cooler 17 may be below the dew point temperature of the mixture. The dew point is the temperature at which the mixture begins to condense. The recycle stream thus may be partially condensed as it exits the cooler 17. This is known as "condensed mode" of operation. The amount of gas and non-condensed vapor in the recycle stream and the velocity of that non-liquid phase should be sufficient to keep the liquid portion of the recycle stream suspended, in order to avoid settling and accumulation of liquid in the recycle line 4. As disclosed by Rhee et al. in U. S. Patent 4,933,149, a deflector device 23 can be designed and positioned in the bottom of the reactor 1 to permit stable operation with or without partial condensing of the recycle stream in line 4.

15 In accordance with this invention the partially condensed recycle stream which exits the cooler 17 is separated into two or more streams. The separation is conducted in a segment 22 of the recycle conduit including an elbow, bend, tee or any other splitter which will separate at least one slip stream, with or without achieving liquid enrichment in the slip stream line 19. By varying the design and placement of the conduit segment 22, the "slip stream" line 19 (sometimes herein called a bypass or a bypass line) can be enriched in liquid content relative to the primary exit stream. In particular line 19 preferably contains 5 to 30 percent of the material in the total recycle stream. By causing the separation to occur at an elbow, bend, tee or other splitter, an enrichment occurs of the liquid content in the small or slip stream (bypass) in line 19. This is due to the difference in momentum between the lower density vapor phase and the higher density liquid phase as they strike the outside radius of the splitter (conduit segment 22), to be explained further with respect to **Figure 2**. The stream in line 19, which has preferably been enriched in liquid content, may be re-injected into the reaction zone of the fluidized bed at one or more locations 20 above the gas distributor grid

-13-

plate 7. In this manner a large quantity of the condensed liquid exiting the cooler can be injected directly into the fluidized bed at levels above the distributor plate without separating the gas and liquid phases using mechanical equipment. The re-injection point of the stream in line 19 may be at multiple locations around the circumference of the fluidized bed and at multiple locations along the axis of the fluidized bed. The locations are chosen to insure rapid dispersion and vaporization of the relatively cool liquid contained in the two-phase stream in line 19. Flow in line 19 may be further controlled by valve 21. In particular, a preferred practice is to manipulate valve 21 to maintain a desired pressure differential of up to 10 psi, preferably 0.01 to 3 psi, between inlet location 20 and the point of entry into the reactor of line 3, the point lower in the bed having the higher pressure. Line 3 may extend into the reactor. In a typical large commercial fluidized bed polyolefin reactor, having a straight section of perhaps 50 feet in height, the lowest re-injection point will be at least 12 inches above the gas distribution plate 7. Re-injection should be in a zone of the fluidized bed where it will vaporize quickly, and usually this is in the lower half, preferably the lower third, of the bed. In addition, it is preferably injected above the product discharge level illustrated by product discharge line 8. However, in principle, the recycle fluid may be re-injected anywhere in the fluidized bed. We prefer that it be at one or more points in the lower third of the bed, for example 8-10 feet above the gas distribution plate.

The relative liquid enrichment of the usually smaller two-phase stream in line 19 can be affected by the velocity of the bulk stream exiting the cooler 17 and also by the density difference between the vapor and liquid phases. The velocity is determined partly by the physical dimensions of the recycle line and the design and operating characteristics of the compressor 16. As disclosed by Jenkins, et al. (see claims 21 and 22) in U. S. Patent 4,588,790, the addition of inert components can be used to adjust the dew point of the recycle stream mixture. With respect to this invention, as the difference between the density of the condensed liquid phase

-14-

and the density of the vapor phase is increased, the enrichment of liquid in the preferably small secondary recycle stream in line **19** is increased. The densities of the liquid and vapor phases change as the composition of the recycle stream is changed. The densities may be manipulated by the addition or removal of more volatile or less volatile (i.e. more dense and/or less dense) chemical components to the recycle stream or reactor. Thus the inerts added to promote condensation may be selected also to enhance the enrichment of liquid into the secondary recycle stream in line **19** by assuring a significant difference in densities. Also variations in the operating conditions within the reactor **1**, depending upon the catalyst type being supplied through line **6**, and the raw materials being supplied through line **18**, will alter the density difference between the vapor and liquid phases exiting the cooler **17**. The specific operating conditions are generally chosen and controlled to be nearly constant and uniform values to produce a consistent desired product which exits the system from line **14**.

A preferred elbow-type splitter (conduit segment **22**) is illustrated further in **Figure 2**. **Figure 2** is an enlargement of the conduit segment **22** of **Figure 1**, and shows a preferred configuration wherein partially condensed recycle fluid enters from cooler **17** and is split into two streams, a primary stream which enters line **3** and a secondary stream which proceeds through line **19**. Line **19** is connected to the outside curve **24** of conduit segment **22**, downstream of a settling chamber **25**. The particular dimensions and curvatures of the conduit segment **22** which affect its efficiency as a fluid splitter may vary with product properties and process parameters as well as desired recycle rates. Generally, the secondary exit line **19** will preferably have a diameter from 5% to 20% of that of primary exit line **3**, and settling chamber **25** will have a diameter larger than that of line **19**, from 10% to 30% of primary exit line **3**. The illustrated settling chamber **25** has a downstream wall **29** to provide an obstacle to the free passage of liquid into line **19**.

-15-

A variant of settling chamber **25** is shown in **Figure 3**, which is further enlarged and contains a computer-generated illustration of the accumulation of liquid in stagnant region **27** of settling chamber **26**. In this version, downstream wall **29** is substantially vertical as depicted – that is, in a plane transverse to the flow in line **4** (**Figure 1**) coming from cooler **17** -- as contrasted with the version illustrated in **Figure 2**. Stagnant region **27** is shown with dotted lines; it represents the region in which liquid accumulates for transport into line **19** and beyond to the fluidized bed as described with respect to **Figure 1**.

The computer analysis depicted graphically in **Figures 3** and **4** reveals that the liquid content of the collection stream is enriched. Results are presented below in **TABLE 4**. Liquid collection efficiencies of 24.00 to 28.82% were obtained for PE (polyethylene) operation, with a feed mixture containing 7.65 wt% liquid. A similar analysis was done for PP (polypropylene) operation with a feed mixture containing 15.6 and 24.9 wt% condensed liquid. The collection efficiency of the liquid droplets into the bypass stream is relative to the total amount of liquid which exits the cooler **17**. A vapor rate through the bypass stream is also computed. An enrichment of liquid into the bypass stream occurs when the weight percentage of liquid in the bypass stream exceeds that in the mixture exiting the cooler **17**. In the following tables, the “bypass stream enrichment ratio” therefore represents the amount of liquid in the slip stream (bypass stream) compared to the amount leaving the cooler **17**. PP liquid collection efficiencies of 20.30 to 24.20% were obtained. These are shown in **Table 5**. The collection efficiency is strongly correlated with droplet size. As shown in **Tables 4** and **5**, splitters can be designed to achieve liquid enrichments in the bypass streams in excess of 1.1 times the liquid content of the stream entering the splitter.

MODEL AND GEOMETRY ASSUMPTIONS

The FLUENT software program (Fluent, Inc., Lebanon, NH) computed vapor and liquid flow distribution within the piping and elbow region. The SIMPLE (semi-

-16-

implicit method for pressure-linked equations) algorithm was employed along with the automatic grid generation features of the Unstructured Mesh Version of FLUENT.

- 5 A steady state model considered conservation of mass and momentum. It employed a standard k-e turbulence model with 5% inlet intensity. This lower level of turbulence was used since the flow profile in the Cycle Gas piping upstream of the elbow may be assumed to be well defined and relatively uniform. **Table 1** includes results for a 3-dimensional geometry. An abrupt 90° elbow is
- 10 illustrated in **Figures 9** and **10**. An ASME class B16.9 90° elbow with a rectangular bypass duct is represented in **Figures 11** and **11a**. In **Figures 9, 10,** and **11**, the inlet diameter is 40.25 and the diameter of exit line **3** is also 40.25. In **Figure 11**, note that the center of rectangular bypass line **53** is at the same level as the center of inlet **4**.

15

TABLE 1. CYCLE PIPING AND BYPASS SLIP STREAM COLLECTION DEVICE GEOMETRY

20	Device Description	Bypass Device Dimensions (inches)		Inlet Cycle Pipe Cylindrical Diameter (inches)	Reference Figures
25	2-dimensional Elbow with Settling Chamber with Collection Nozzle	Chamber	18.00	34.50	3, 4, 5, 6b, 7, 8
		Nozzle	4.00		
30	3-dimensional Abrupt Elbow with Collection Nozzle	Nozzle	12.00	40.25	9, 10
35	3-dimensional ASME B16.9 Cylindrical Pipe and Elbow with Rectangular Collection Duct	Duct Width	18.0	40.25	11
		Duct Height	9.0		

DISCRETE LIQUID PHASE DROPLET MODEL

- Liquid droplet particle tracking was done using the Lagrangian discrete phase
- 40 approach. The Lagrangian particle tracking feature allows for the computation of

-17-

the trajectories of groups of individual droplets. This feature accounts for droplet inertia, drag, buoyancy and gravity forces. The drops were injected across the inlet boundary at evenly spaced injection points.

- 5 As shown in **Figure 4**, defining zones along the wall and at exit boundaries allowed the monitoring of position for the droplets which were captured. All of the wall zones **A, B, C, D, E, F, G**, and **H** were assigned the property to capture any liquid droplets whose trajectory terminated there. Droplets in zones **C, D, E, F, G**, and **L** would be collected. The liquid collection efficiency was defined by
- 10 dividing the droplet quantity in these zones by the total injected. Droplets in contact with zone **B**, the bottom of the Cycle Gas pipe, could possibly be re-entrained into the mixture.

- Graphical fluid phase profiles were used to qualitatively assess liquid collection efficiency. A minimum mean droplet size of 104 microns (0.0041 inch) and a
- 15 maximum droplet size of 312 microns (0.0123 inch) were used. The enrichment results are based on the average of the calculations for the two droplet sizes. FLUENT post-processing using particle tracking was conducted using both the droplet sizes.

- 20 After solving for the vapor velocity, pressure and turbulence profiles for the continuous phase, inert liquid droplets were injected at the inlet boundary. **Figure 5** illustrates a typical polyethylene drop trajectory for 8 drops of size 0.0041 inch (104 micron) with a velocity of 35 ft/sec.. Droplet size and inertia were found to
- 25 be strongly correlated with capture efficiency of the elbow device. **Figures 4** and **6** illustrate polyethylene process recycle velocity profiles with 0.0041 inch and 0.0123 inch elbow inlets respectively, at different velocities. **Figures 7** and **8** are similar drop trajectory results for a polypropylene process.

- Figure 9** illustrates a right angle elbow having a bypass line **50** slightly below the
- 30 level of inlet line **4**, **Figure 10** shows a bypass line **52** slightly above inlet line **4**, and **Figure 11** shows a rectangular bypass duct **53** having a center at the same

level as the center of inlet 4, as in ASME model B16.9. **Figure 11a** shows the cross section of bypass duct 53, having dimensions of 9 and 18 inches. Preferably, the bypass duct in any of our configurations will have a hydraulic diameter of 5 to 30%, more preferably 5 to 20%, of the diameter of the primary outlet. All of these configurations are satisfactory in our invention.

MODEL FLUID PROPERTY ASSUMPTIONS

For analyses, reactor fluid properties similar to those of common commercial homopolymers of ethylene and propylene were assumed. These are shown below in **TABLE 2**. The FLUENT continuous phase was represented by the Cycle Gas vapor properties.

TABLE 2. CYCLE GAS FLUID PROPERTIES NEAR REACTOR INLET

Polymer	Polyethylene	Polypropylene	
		A	B
Pressure, psia	374.4	556.2	501.2
Temp, deg C	53.0	63.1	57.2
Liquid wt%	7.65	15.60	24.96
Density, lb/ft ³			
mixture	1.95	5.51	5.25
vapor	1.80	4.80	4.14
liquid	38.6	26.4	27.30
Viscosity, cp			
vapor	0.016	0.014	0.013
liquid	0.180	0.035	0.044

MODEL BOUNDARY CONDITIONS AND COMPUTATIONAL MODEL

RESULTS

Referring to **Figure 4**, at steady state, a uniform velocity isothermal vapor enters the left side of the computational domain. Some fluid exits through the chamber and collection nozzle (zone E and outlet L). Most of the fluid is turned at the elbow and travels vertically. It exits at the top boundary (outlet zone K). A velocity specification and reference pressure was used at the inlet boundary (zone J). Pressure and/or velocity specifications were employed at both of the exit boundaries (zones K and L).

The amount of vapor exiting through the collection nozzle (zone **E** and outlet **L**) is a function of the pressure difference between the two exit boundaries (zones **K** and **L**). Outlet **L** is attached to recycle piping (slip stream line **19**) to transport the mixture to an upper portion of the fluidized bed **2** (**Figure 1**). The control of the flow bypassing the Reactor bottom head **23** and plate **7** may be made by varying the resistance in line **19** and valve **21**.

The liquid droplet recovery information is summarized below in **Table 3**. The liquid droplet recovery was defined by dividing the droplet quantity in zones **C**, **D**, **E**, **F**, **G**, and **L** by the total injected. The vapor recovery is the percent of total vapor flow which exits through the collection device at the elbow. Since the liquid droplet recovery exceeds the vapor recovery, a net enrichment of liquid occurs in the secondary stream exiting the collection nozzle.

TABLE 3. LIQUID DROPLET RECOVERY FOR 1,000 TRAJECTORIES - ELBOW WITH SETTLING CHAMBER AND BYPASS DUCT - FIGURE 4

	Polymer	Inlet Liquid (wt. %)	Inlet Velocity (feet/sec)	Bypass Vapor Recovery (% of inlet)	Bypass Droplet (microns)	Bypass Liquid Recovery (% of inlet)
20						
25	Polyethylene	7.65	35	19.59	104	24.00
	Polyethylene	7.65	35	19.59	312	27.90
	Polyethylene	7.65	55	19.61	104	24.40
	Polyethylene	7.65	55	19.61	312	28.82
	Polypropylene	15.60	25	17.38	104	20.30
	Polypropylene	15.60	25	17.38	312	22.30
30	Polypropylene	15.60	35	17.28	104	20.30
	Polypropylene	15.60	35	17.28	312	22.50
	Polypropylene	24.96	25	18.45	104	21.50
	Polypropylene	24.96	25	18.45	312	23.70
	Polypropylene	24.96	35	18.44	104	21.70
35	Polypropylene	24.96	35	18.44	312	24.20

PE liquid droplet population distributions are illustrated in **Table 4** for polyethylene and **Table 5** for polypropylene. **Figure 5** illustrates typical liquid droplet trajectory profiles for a subset case of only eight liquid droplets.

TABLE 4. LIQUID DROPLET DISTRIBUTION FOR POLYETHYLENE CYCLE GAS

5	Vapor Density lb/ft ³	1.80	1.80	1.80	1.80
	Liquid Density lb/ft ³	38.60	38.60	38.60	38.60
10	Condensed Liquid weight percent	7.65	7.65	7.65	7.65
	Cycle Pipe Velocity feet/sec	35.00	35.00	55.00	55.00
15	Droplet Mean Size microns	104.00	312.00	104.00	312.0
20	Pressure Differential (Outlet - Bypass) (lb/in ²)	1.0	1.0	2.3	2.3
	Droplet Distribution by Zone (reference Figure 4) (% of 1,000 trajectories)				
25	A	0.00	0.00	0.00	0.00
	B	3.80	13.00	2.00	6.80
	C	0.00	1.20	0.00	0.20
	D	1.10	1.10	0.60	1.40
	E	1.20	1.30	0.90	0.90
30	F	0.00	0.30	0.00	0.70
	G	2.00	5.30	1.90	6.30
	H	5.60	16.40	5.40	17.00
	J	0.00	0.00	0.00	0.00
	K	66.60	42.70	68.20	46.90
35	L	19.70	18.70	21.00	19.80
	Bypass percentage of Inlet				
	Vapor	19.59	19.59	19.61	19.61
	Liquid	24.00	27.90	24.40	28.82
40	Bypass Liquid Enrichment (weight ratio to Inlet)	1.21	1.38	1.22	1.44

-21-

TABLE 5. LIQUID DROPLET DISTRIBUTION FOR POLPROPYLENE CYCLE GAS --
ELBOW WITH SETTLING CHAMBER AND BYPASS DUCT
FIGURES 7 and 8

5	Vapor Density (lb/ft ³)	4.80	4.80	4.80	4.80	4.14	4.14	4.14	4.14
	Liquid Density (lb/ft ³)	26.40	26.40	26.40	26.40	27.30	27.30	27.30	27.30
10	Inlet Liquid (weight %)	15.60	15.60	15.60	15.60	24.96	24.96	24.96	24.96
	Inlet Velocity (ft/second)	25.	25.	35.	35.	25.	25.	35.	35.
15	Bypass Liquid Droplet Size (microns)	104.	312.	104.	312.	104.	312.	104.	312.
	Pressure Differential (Outlet-Bypass) (lb/in ²)	0.9	0.9	1.7	1.7	0.9	0.9	1.7	1.7
20	Droplet Distribution by Zone (reference Figure 4) (% of 1,000 trajectories)								
	A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	B	3.00	9.90	1.90	6.20	3.50	11.20	2.20	7.10
25	C	0.00	1.10	0.00	0.40	0.00	1.30	0.00	0.70
	D	1.10	1.20	0.60	1.60	1.30	1.30	0.80	1.40
	E	0.90	1.00	1.60	1.10	0.90	0.90	1.40	1.10
	F	0.00	0.10	0.00	0.20	0.00	0.00	0.00	0.30
	G	1.20	1.70	1.30	1.90	1.30	1.90	1.40	2.10
30	H	2.90	6.80	2.70	6.70	3.30	7.80	3.00	7.70
	J	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	K	73.80	61.00	75.10	64.40	71.70	57.30	73.10	61.00
	L	17.10	17.20	16.80	17.50	18.00	18.30	18.10	18.60
35	Bypass percentage of Inlet								
	Vapor	17.38	17.38	17.28	17.28	18.45	18.45	18.44	18.44
	Liquid	20.30	22.30	20.30	22.50	21.50	23.70	21.70	24.20
40	Bypass Liquid Enrichment (weight ratio to Inlet)								
		1.14	1.23	1.15	1.24	1.12	1.20	1.13	1.22

This analysis reveals that it is feasible to collect about 20.30 to 24.20% of the liquid in the recycle stream into the smaller split stream, and to increase the ratio of liquid to gas in the smaller stream as compared to the ratio in the main recycle stream. Liquid collection efficiency is strongly correlated with droplet size and density, and the difference in momentum between the vapor and liquid phases.

COMPUTATIONAL MODEL CONCLUSIONS

Two- and three-dimensional models were developed for the recycle fluid piping elbow. Results were presented from the FLUENT Unstructured Mesh software
5 program. Liquid droplet particle tracking was done using the Lagrangian approach. Recycle fluid properties typical of commercial polyethylene and homopolypropylene processes were assumed in the analysis. For the polyethylene case, recycle velocities of 35 and 55 ft/sec were considered, with a liquid condensation level of 7.65 wt%. The polypropylene cases were at 15.6 wt% and
10 24.9 % condensing, each comparing velocities of 25 and 35 ft/sec.

In this analysis the vapor recovery through the collection device was maintained below 21% of the incoming flow rate. This amount of bypass around the Reactor distributor plate may be tolerated without disrupting the fluidization of the
15 polymer bed.

When comparing the PE results at increasing recycle line velocities, about the same liquid droplet collection efficiency was observed. For the polyethylene system, as the mean droplet size was increased from 104 to 312 microns, the
20 liquid droplet recovery increased by about 4%. The polypropylene system has a smaller difference in density between the vapor and liquid phases. Accordingly the momentum difference is smaller between the phases. The improvement in liquid collection efficiency with increasing liquid droplet size is smaller.

25 The analysis reveals that it is feasible to collect about 20% to about 29% of the liquid into the smaller split stream with a differential pressure – that is, the difference in pressure between the points of entrance into the reactor of the smaller split stream and the larger stream of line 3 -- of less than 3 psi. Liquid collection efficiency is strongly correlated with droplet size and momentum
30 difference between the vapor and liquid phases.

SPLITTER DESIGN

As indicated above, the splitter is preferably designed more or less as illustrated in **Figures 2, 3, 9, 10, or 11** using an elbow having a small line **19** on its large radius side and most preferably a settling chamber **25** defined by a take-off of larger diameter than the small line **19**. The constriction to line **19** can be perpendicular to flow as wall **29** in **Figure 3** or somewhat tapered or gradual as in **Figure 2**, and line **19** may be rectangular in cross section as seen in **Figure 11a**. As seen in the velocity and droplet distribution data above, use of a settling chamber will result in an accumulation of liquid available to be discharged with the slip stream, giving it a higher ratio of liquid to gas than the incoming recycle stream or the primary recycle stream. The design illustrated in **Figure 3**, wherein the settling chamber has a vertical dead-end wall **29**, generates a slip stream in line **19** relatively highly enriched in liquid but relatively low in volume; tapering wall **29** as in **Figure 2** will result in a higher volume of fluid having a lower liquid percentage.

Referring to **Figure 12**, parallel discharge tanks, which include conduits and valves, may be intermittently operated in an alternate sequential mode as disclosed by Aronson in U.S. Patent 4,621,952. The interconnecting conduits, isolation valves and vents to the upper region of the fluidized bed are operated to minimize the loss of valuable gas with the product solid.

During a discharge process, the polymer product and raw material fluids exit through either lines **8** or **8'** into either vessel **10** or **10'**. This product removal obtained by opening either valves **9** or **9'** when the downstream vessel is initially at a lower pressure than the reactor vessel **1**. The choice for product withdraw vessel as **10** or **10'** is alternated, while the parallel vessel serves as a pressure equalization vessel. Thus the discharge cycle vessel **10** receives the solid and

-24-

fluid from the reactor **1**. Vessel **10'** contains substantially no solid at this point. It is available to receive the subsequent pressure equalization vent from vessel **10**.

For one discharge cycle, the polymer product and fluids from the reaction vessel **1** enter the active discharge vessel **10**. The vent valve **65** in conduit **62** interconnecting vessel **10** with the upper portion of the fluidized bed **2** is open, thus allowing fluid to return to the reactor **1**. Valves **9** and **65** are then closed to isolate vessel **10** from the reaction vessel **1** at pressure approximately equal to that in the reaction vessel. The polymer product settles into vessel **10**. The valve **66** in the conduit **61** connecting with the parallel vessel **10'** is opened and the pressures allowed to equalize between the vessels **10** and **10'**. Valve **61** interconnecting vessels **10** and **10'** is then closed. Fluid is thus transferred from vessel **10** to vessel **10'** during the pressure equalization. Upon a subsequent alternate discharge cycle into vessel **10'** a portion of that equalization fluid is vented back into the reaction vessel **1**. This venting and pressure equalization provides an attractive mechanism for the recovery of valuable unreacted monomers and inert materials from the semi-batch discharge system without the use of mechanical equipment such as compressors and pumps.

The polymer product is then transferred from vessel **10** by gravity and pressure equalization into vessel **12**. Valve **11** is then closed to isolate vessel **12** from vessel **10**. After the polymer product settles into vessel **12**, the valve **63** in the conduit **60** connecting with the parallel vessel **12'** is opened and the pressures allowed to equalize between the vessels **12** and **12'**. Fluid was thus transferred from vessel **12** to vessel **12'** during the pressure equalization. Upon a subsequent discharge cycle into vessel **10'** and polymer product transfer into vessel **12'** a portion of that equalization fluid is vented back into the discharge vessel **10'**. On the next discharge event into vessel **10'** a portion of the fluid in vessel **10'** vents back to the reactor vessel **1** through the conduit **64'** and valve **65'**.

-25-

After additional equalization venting and polymer product transfer steps through conduit **14**, the polymer product and remaining fluids are processed by downstream equipment. Since the fluids contain valuable raw materials, it is economically desirable to minimize their net removal from the reactor vessel **1**.

5 The product removal capacity of the production facility is thus determined by the time necessary to economically complete a discharge and pressure equalization cycle, and the overall production capacity of the reactor system may be limited by the efficiency of product removal. This is especially so as higher and higher condensing ratios are utilized to improve the rate of removal of the process heat of
10 reaction. The raw material efficiency of the process is affected by the minimum pressure which is obtainable by the steps of vessel pressure equalization. Achieving a lower equalization pressure affords a reduction in the raw material usage of the facility.

15 Operation of the reaction system with a partially condensed recycle through conduit **3** can result in liquid being present in the lower regions of the fluidized bed **2**. When substantial amounts of a liquid phase are also intermittently removed with the solid and gas from the fluidized bed **2** to the discharge vessels **10** and **10'**, the time duration of the discharge process steps can increase. This is
20 because as the pressure is reduced during the venting and pressure equalization stages of the discharge process, a portion of the liquid phase will vaporize. This liquid vaporization increases the final pressure and the time necessary to complete all the venting and pressure equalization steps between the discharge vessels and downstream processing equipment. The increase in time to complete the necessary
25 steps of the semi-batch discharge process, reduces the product removal capacity of the facility.

The cycle time of the semi-batch discharge process can be reduced by inhibiting the discharge vessel venting steps from reaching pressure equalization. However,
30 if the pressure is not equalized, then a larger portion of the discharged fluids will

-26-

leave the reaction system. Thus a larger quantity of fluid materials is lost or must be processed by downstream operations for recovery. The raw material efficiency of the process is effected by the minimum pressure which is obtainable by the steps of vessel venting and pressure equalization. Achieving a lower equalization pressure affords a reduction in the raw material usage of the production facility. The optimal product removal capacity of the facility is thus determined by the time necessary to economically complete a discharge and pressure equalization cycle.

In the practice of this invention conventional pressure measurement and transmitter devices are installed on the discharge vessels **10**, **10'**, **12** and **12'**. An increase in equalization pressure of the discharge vessels is observed as the liquid content in streams **8** and **8'** is increased. Any vapor liquid separating equipment can be used to reduce the liquid content of the recycle stream **3**. It is well known by those skilled in the art of vapor liquid separation that mechanical devices such as impingement demisters and hydrocyclones can be used to accomplish vapor liquid separation.

In the preferred embodiment of this invention the vapor liquid separation of the recycle stream exiting the cycle gas cooler **17** is achieved using the inertial bypass stream **19**. During "condensed mode" operation, when the equalization pressure in the discharge vessels is observed to increase, the bypass valve **21** is opened and the flowrate of enriched liquid bypass stream **19** is increased while the liquid content of the recycle stream **3** is reduced. This serves to reduce the liquid content in the polymer product discharge streams **8** and **8'**. The magnitude of the pressure being measured in the discharge vessels **10**, **10'**, **12**, **12'** is thereby reduced and the rate of product transfer is thereby improved.

This invention reduces the quantity of liquid which can exit the fluidized bed **2** with the polymer product into vessels **10** and **10'** when operating in the condensed

-27-

mode. The bypass streams can be returned to the reactor fluidized bed **2**, at an elevation above that of the polymer product discharge lines **8** and **8'**. The separation of the recycle stream is conducted such that the liquid content of the bypass streams are enriched and the liquid content of the primary recycle stream **3** is reduced. By opening valve **21** and bypassing a liquid enriched portion of the recycle flow into stream **19**, a lesser quantity of liquid is returned to the bottom of the reactor through stream **3**. Reducing the liquid content of the recycle stream **3** to the reactor inlet also reduces the liquid content in the fluid mixture exiting from the reactor with the solid polymer product in the discharge streams **8** and **8'**.

10

By practicing this invention with “condensed mode” of operation both the economic penalties of longer duration semi-batch discharge cycles and of increased raw material usage are reduced. Returning the enriched liquid content bypass streams **19** and **20** to the fluidized bed **2**, at a location above the product removal streams **8** and **8'** retains the heat removal production advantages of “condensed mode” operation.

Compared in **Figure 13** are dry and wet discharge events for identical discharge vessels which are operated at equivalent source vessel and sink vessel initial pressure. The wet discharge includes with the solid polymer product a vapor and liquid fluid mixture which comprises 24.66 weight percent liquid. The final equalization pressure is higher for the wet discharge event as compared with the dry discharge. The time duration to equalize pressure for the wet discharge event is longer than for the dry discharge event. The product removal capacity is thereby lower and the raw material loss higher when liquid is discharged along with the vapor and solid flow.

EXAMPLES

-28-

In order to provide a better understanding of the present invention the following examples are provided. They represent computer simulations of commercial scale operating facilities for the gas phase fluidized bed exothermic production of polyethylene and polypropylene.

5

Example 1

A fluidized bed polymerization reactor system similar to that of **Figure 1** is producing linear low density polyethylene which contains about 10 weight percent copolymerized hexene. Referring to **Figure 1**, the recycle stream in line **4** contains a mixture of hydrogen, nitrogen, methane, ethane, ethylene, hexene and hexane. The pressure 374.4 psia and temperature 53.0°C at the exit of the external cooler **17** yields a bulk recycle stream containing 7.65 weight percent liquid. The entrained droplet size of the liquid is in the range of 104 to 312 microns or 0.0041 to 0.0123 inches. The liquid phase is rich in hexene and hexane and has a density of 38.6 lb/ft³. The vapor phase is rich in the more volatile components of the mixture and has a density of 1.80 lb/ft³. As illustrated in **Figure 1** the small bypass or slip stream in line **19** is designed to contain 19.59 percent of the inlet vapor (the gas phase of the inlet fluid) with a 0.9 psi differential pressure. The velocity of the fluid is 35 feet per second at the exit of the cooler **17** and upstream of the separation elbow. The small stream **19** contains an average of 25.95 percent of the liquid entering the inlet. The average enrichment is thus 1.29 times the liquid content of the bulk recycle stream exiting the cooler **17**.

25 Example 2

A fluidized bed polymerization reactor is producing linear low density polyethylene which contains about 10 weight percent polymerized hexene. Referring to **Figure 1**, the recycle stream **4** contains a mixture of hydrogen, nitrogen, methane, ethane, ethylene, hexene and hexane. The pressure 374.4 psia

-29-

and temperature 53.0°C at the exit of the external cooler **17** yields a recycle stream containing 7.65 weight percent liquid. The liquid phase, rich in hexene and hexane, has a density of 38.6 lb/ft³. The vapor phase is rich in the more volatile components of the mixture and has a density of 1.80 lb/ft³. As illustrated in **Figure 1**, the small stream **19** is designed to contain 19.61 percent of the inlet vapor with a 2.3 psi differential pressure. The velocity of the recycle stream is 55 feet per second at the exit of the cooler **17** and upstream of the separation elbow. The small stream **19** contains an average of 26.61 percent of the inlet liquid. The average weight ratio enrichment of the small stream **19** is thus 1.33 times the liquid content of the bulk recycle stream exiting the cooler **17**.

Example 3

A fluidized bed polymerization reactor is producing propylene homopolymer. Referring to **Figure 1**, the recycle stream **4** contains a mixture of hydrogen, nitrogen, propylene and propane. The pressure is 556.2 psia and temperature of 63.1°C at the exit of the external cooler **17** yield a recycle stream containing 15.60 weight percent liquid. The liquid phase, rich in propylene and propane, has a density of 26.4 lb/ft³. The vapor phase is rich in the more volatile components of the mixture and has a density of 4.80 lb/ft³. As illustrated in Fig. **1** the small stream **19** is designed to contain 17.38 percent of the inlet vapor with a 0.9psi differential pressure. The fluid velocity is 25 feet per second at the exit of the cooler **17** and upstream of the separation elbow. The small stream **19** contains an average of 21.3 percent of the inlet liquid. The average weight ratio enrichment is thus 1.18 times the liquid content of the bulk recycle stream exiting the cooler **17**.

Example 4

A fluidized bed polymerization reactor is producing propylene homopolymer. Referring to **Figure 1**, the recycle stream **4** contains a mixture of hydrogen, nitrogen, propylene and propane. The pressure (556.2 psia) and temperature (63.1°C) at the exit of the external cooler **17** yield a recycle stream containing 15.60 weight percent liquid. The liquid phase, being rich in propylene and propane, has a density of 26.4 lb/ft³. The vapor phase is rich in the more volatile components of the mixture and has a density of 4.80 lb/ft³. As illustrated in **Figure. 1** the small stream **19** is designed to contain 17.28 percent of the inlet vapor with a 1.7 psi differential pressure. The fluid velocity is 35 feet per second at the exit of the cooler **17** and upstream of the separation elbow. The small stream **19** contains an average of 21.4 percent of the inlet liquid. The average weight ratio enrichment is thus 1.19 times the liquid content of the bulk recycle stream exiting the cooler **17**.

Example 5

A fluidized bed polymerization reactor is producing propylene homopolymer. Referring to **Figure 1**, the recycle stream **4** contains a mixture of hydrogen, nitrogen, propylene and propane. The pressure 501.2 psia and temperature 57.2°C at the exit of the external cooler **17** yields a recycle stream containing 24.96 weight percent liquid. The liquid phase being rich in propylene and propane has a density of 27.3 lb/ft³. The vapor phase, being rich in the more volatile components of the mixture, has a density of 4.14 lb/ft³. As illustrated in Fig. 1 the small branch stream **19** is designed to contain 18.45 percent of the inlet vapor with a 0.9 psi differential pressure. The fluid velocity is 25 feet per second at the exit of the cooler **17** and upstream of the separation elbow. The small stream **19** contains an average of 22.60% of the inlet liquid. The average weight ratio

enrichment is thus 1.16 times the liquid content of the bulk recycle stream exiting the cooler 17.

Example 6

5

A fluidized bed polymerization reactor is producing propylene homopolymer. Referring to **Figure 1**, the recycle stream 4 contains a mixture of hydrogen, nitrogen, propylene and propane. The pressure of 501.2 psia and temperature 57.2°C at the exit of the external cooler 17 yields a recycle stream containing
10 24.96 weight percent liquid. The liquid phase, being rich in propylene and propane, has a density of 27.3 lb/ft³. The vapor phase being rich in the more volatile components of the mixture, has a density of 4.14 lb/ft³. As illustrated in **Figure 1** the small branch stream 19 is designed to contain 18.44 percent of the inlet vapor with a 1.7 psi differential pressure. The fluid velocity is 35 feet per
15 second at the exit of the cooler 17 and upstream of the separation elbow. The small stream 19 contains an average of 22.95 percent of the inlet liquid. The enrichment is thus 1.17 times the liquid content of the bulk recycle stream exiting the cooler 17.

20 Example 7

A 3 dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was analyzed with an abrupt 90 degree elbow. A 12 inch internal diameter slip stream cylindrical pipe was located across from the bottom of the inlet pipe as referred in
25 **Figure 9**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets exiting through the secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by
30 material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 1. The secondary

-32-

bypass slip stream was designed to contain 16.17 percent of the inlet vapor. This design required a 1.0 psi. pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 35 feet per second. The secondary bypass slip stream was computed to

5 contain an average of 25.81 percent of the total inlet liquid. The average weight ratio enrichment was 1.51 times the weight fraction of liquid at the inlet.

Example 8

10 A 3-dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was analyzed with an abrupt 90 degree elbow. A 12 inch internal diameter slip stream cylindrical pipe was located across from the top of the inlet pipe as referred in **Figure 10**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets exiting through the

15 secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 1. The secondary

20 bypass slip stream was designed to contain 15.25 percent of the inlet vapor. This design required a 1.0 psi pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 35 feet per second. The secondary bypass slip stream was computed to contain an average of 29.07 percent of the total inlet liquid. The average weight

25 ratio enrichment was 1.77 times the weight fraction of liquid at the inlet.

Example 9.

A 3-dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was

30 analyzed with an ASME B16.9 specified elbow. An 18 inch wide by 9 inch high rectangular slip stream duct was located across from the center streamline of the

105020 "E42260

-33-

inlet pipe as referred in **Figure 11**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets exiting through the secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 1. The secondary bypass slip stream was designed to contain 20.70 percent of the inlet vapor. This design required a 0.7 psi pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 35 feet per second. The secondary bypass slip stream was computed to contain an average of 36.88 percent of the total inlet liquid. The average weight ratio enrichment was 1.69 times the weight fraction of liquid at the inlet.

15

Example 10.

A 3-dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was analyzed with an ASME B16.9 specified elbow. An 18 inch wide by 9 inch high rectangular slip stream duct was located across from the center streamline of the inlet pipe as referred in **Figure 11**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets exiting through the secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 2. The secondary bypass slip stream was designed to contain 20.79 percent of the inlet vapor. This design required a 1.8 psi pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 55 feet per second. The secondary bypass slip stream

T05020" E422250

-34-

was computed to contain an average of 38.59 percent of the total inlet liquid. The average weight ratio enrichment was 1.73 times the weight fraction of liquid at the inlet.

5 Example 11.

A 3-dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was analyzed with an ASME B16.9 specified elbow. A 18 inch wide by 9 inch high rectangular slip stream duct was located across from the center streamline of the inlet pipe as referred in **Figure 11**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets exiting through the secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 3. The secondary bypass slip stream was designed to contain 18.12 percent of the inlet vapor. This design required a 0.6 psi pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 25 feet per second. The secondary bypass slip stream was computed to contain an average of 35.38 percent of the total inlet liquid. The average weight ratio enrichment was 1.67 times the weight fraction of liquid at the inlet.

25 Example 12.

A 3-dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was analyzed with an ASME B16.9 specified elbow. An 18 inch wide by 9 inch high rectangular slip stream duct was located across from the center streamline of the inlet pipe as referred in **Figure 11**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets

-35-

exiting through the secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 4. The secondary bypass slip stream was designed to contain 18.15 percent of the inlet vapor. This design required a 1.3 psi pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 35 feet per second. The secondary bypass slip stream was computed to contain an average of 30.10 percent of the total inlet liquid. The average weight ratio enrichment was 1.49 times the weight fraction of liquid at the inlet.

Example 13.

A 3-dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was analyzed with an ASME B16.9 specified elbow. An 18 inch wide by 9 inch high rectangular slip stream duct was located across from the center streamline of the inlet pipe as referred in **Figure 11**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets exiting through the secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 5. The secondary bypass slip stream was designed to contain 19.71 percent of the inlet vapor. This design required a 0.7 psi pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 25 feet per second. The secondary bypass slip stream was computed to contain an average of 40.09 percent of the total inlet liquid. The

average weight ratio enrichment was 1.59 times the weight fraction of liquid at the inlet.

Example 14.

5

A 3-dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was analyzed with an ASME B16.9 specified elbow. An 18 inch wide by 9 inch high rectangular slip stream duct was located across from the center streamline of the inlet pipe as referred in **Figure 11**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets exiting through the secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 1. Variations in droplet size were considered to discern the limiting droplet size, below which there was no enrichment of liquid into the secondary bypass slip stream. The secondary bypass slip stream was designed to contain 20.70 percent of the inlet vapor. This design required a 0.7 psi pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 35 feet per second. For a liquid droplet size larger than 20 microns, the secondary bypass slip stream was computed to contain more liquid than the inlet recycle pipe. Thus liquid enrichment into the secondary bypass stream was obtained when the inlet droplet size exceeded 20 microns.

10
15
20
25

Example 15.

A 3-dimensional cylindrical recycle pipe with a 40.25 inch internal diameter was analyzed with an ASME B16.9 specified elbow. An 18 inch wide by 9 inch high rectangular slip stream duct was located across from the center streamline of the

30

-37-

inlet pipe as referred in **Figure 11**. At the inlet to the domain 1,000 liquid droplets were injected throughout the cross section. The fraction of droplets exiting through the secondary bypass slip stream was compared with the fraction exiting the primary outlet. The fraction of vapor exiting the bypass and primary outlet were also compared. The weight fraction of liquid exiting the bypass was computed by material balance and compared with the weight fraction of liquid at the inlet. Operating conditions were identical to those shown in Example 3. Variations in droplet size were considered to discern the limiting droplet size, below which there was no enrichment of liquid into the secondary bypass slip stream. The secondary bypass slip stream was designed to contain 18.12 percent of the inlet vapor. This design required a 0.6 psi pressure difference between the primary outlet and the secondary bypass slip stream. This outlet differential pressure was at an inlet fluid velocity of 25 feet per second. For a liquid droplet size larger than 47 microns, the secondary bypass slip stream was computed to contain more liquid than the inlet recycle pipe. Thus liquid enrichment into the secondary bypass stream was obtained when the inlet droplet size exceeded 47 microns.

Example 16

A fluidized bed polymerization reactor similar to that of **Figure 1** is producing propylene homopolymer. Referring to **Figure 1**, the recycle stream 4 contains a mixture of hydrogen, nitrogen, propylene and propane. The pressure is 501.2 psia and the temperature is 57.2°C at the exit of cooler 17, yielding a recycle stream containing 24.96 weight percent liquid at the cooler exit. The liquid phase is rich in propylene and propane and has a density of 27.3 lb/ft³. The vapor phase is rich in the more volatile species and has a density of 4.14 lb/ft³. As illustrated in **Figure 1**, the small line 19 is designed to contain 19.71 percent of the inlet vapor with a 0.7 psi differential pressure between the primary outlet and the secondary bypass. The recycle stream velocity is 25 feet per second at the exit of the cooler 17 and upstream of the splitter 22. When the valve 21 is closed in bypass stream

105020 "E-H-2250

-38-

19, some amount of liquid is removed from fluidized bed 2 as the polymer product is withdrawn through line 8 into vessel 10. The liquid vaporizes in vessel 10, which increases the pressure in vessel 10. This back pressure inhibits the flow of polymer product through line 8. The polymer production capacity of the facility is thus limited by the ability to remove polymer product through line 8. Opening the valve 21 in the bypass line 19 causes the amount of liquid entering the fluidized bed 2 through line 3 to be reduced. The secondary bypass slip stream (line 19) was computed to contain an average of 40.09 percent of the total inlet liquid. Bypass line 19 achieves an enrichment of liquid content of 1.59 times the liquid content of the stream exiting the cooler 17, and the production and removal of polymer product is increased by 18%.

Example 17

15 A fluidized bed polymerization reactor with parallel and interconnected discharge tanks similar to that of **Figure 12** was producing propylene homopolymer. The recycle stream 4 at a pressure of 490 psia, contained a mixture of hydrogen, nitrogen, propylene and propane. The pressure at the discharge lines 8 and 8' was 492.6 psia. The pressure was 501.2 psia at the exit of the external cooler 17. At a temperature below the dew point of 61°C there was liquid present in stream 67, at the exit of the cooler 17.

When operating in “condensed mode”, with the recycle stream 3 containing some liquid, then a portion of the liquid was carried from fluidized bed 2 as the polymer product was intermittently withdrawn through streams 8 and 8'. For this example, streams 8 and 8' were located less than 2 feet above the top elevation of the distributor plate 7. We have found that the relative concentration of liquid to vapor in the discharge streams 8 and 8' exceeds that in stream 3. Comparisons are made in **Table 6** with increasing levels of liquid in stream 8 or 8', which enters

-39-

the discharge vessels **10** or **10'**. Discharge conditions and the resulting time duration of the discharge process are displayed in **Table 6**.

For the test cases of this Example 17, the two phase fluid recycle stream exiting the cooler **17** was separated into a primary recycle stream **3** and a bypass stream **19**. The bypass stream was returned to the reactor fluidized bed **2**, at an elevation above that of the polymer product discharge streams **8** and **8'**. The separation was conducted such that the liquid content of the bypass stream was enriched and the liquid content of the primary recycle stream was reduced. The test cases with reduced liquid at the reactor inlet, resulted in reduced liquid in the fluid mixture exiting with the solid polymer product in the discharge streams **8** and **8'**.

During a discharge process, the polymer product and raw material fluids exit through either line **8** or **8'** into either vessel **10** or **10'**. This product removal obtained by opening either valve **9** or **9'** when the downstream vessel **10** or **10'** is initially at a lower pressure than the reactor vessel **1**. During the solid and fluid transfer into the vessel, a vent valve **65** or **65'** is opened, allowing a portion of the fluid in the vessel to be returned to the reactor vessel **1**.

The choice for product withdraw vessel as **10** or **10'** is alternated. The parallel vessel, which did not receive the polymer product, would subsequently serve as a pressure equalization vessel with the vent from the discharge vessel. The time duration to equalize and final pressure was determined and recorded in **Table 6**.

A small amount of absorbed gas is also evolved from the solid polymer product during the discharge process. The quantity of gas dissolved in the solid product and evolved during the discharge process is dependent upon the crystallinity, particle size, molecular weight and rheological properties of the polymer product, the physical properties of the absorbate, and the composition, temperature and pressure of the surrounding fluid.

For the four test cases in this Example 17 the polymer product had a solid phase density of 56.4 lb/ft³. For a given semi-batch discharge cycle, the solid polymer product occupied a volume of 17.17 ft³ in the vessels. Each discharge event removed 968 lb of solid polymer product from the reactor fluidized bed **2**. The balance of volume was occupied by raw material fluids. These fluids were in the vapor and optionally liquid phase. They comprised unreacted monomers and inert species. The total volume in the interconnecting system for vessels **10** and **10'** was 94% of the available volume for vessels **12** and **12'**.

10

The total time duration of the discharge process is exemplified in **Table 6**. Cases with multiple venting and equalization steps are included. Time duration for valves to open and close are included in each event. The total time duration includes several sequential batch steps. The first step is the polymer discharge and venting into vessel **10**. The pressure equalization with vessel **10'** was the second step. The third step was the transfer of polymer and fluids into vessel **12**. This step includes the venting and pressure equalization between vessels **10** and **12**. The vent equalization between vessel **12** and **12'** was the fourth step in the discharge process.

20

The venting and transfer through lines **14** or **14'** to downstream processing equipment was the final step in the discharge process. In all test cases of this Example a vent through lines **14** or **14'** was included to lower the pressure in vessel **12** or **12'** to 140 psia, prior to the transfer of the solid polymer product. The equipment into which the venting was directed and transfer was completed had an available volume of 27 times the available volume in vessel **10**.

25

The product removal capacity of the production facility is limited by the time necessary to economically complete a discharge and pressure equalization cycle. When operating in "condensed mode", with the discharge of fluid containing

30

-41-

some liquid, the time duration necessary to complete the intermittent discharge process was shown to increase as the quantity of liquid in the discharge streams **8** and **8'** was increased.

- 5 In this Example 17 the product removal capacity of the discharge system decreased from 17,744 to 16,933 lb polymer per hour as the liquid concentration in streams **8** or **8'** increased from 15.59 to 29.61 weight percent.

Also included in **Table 6** is a summary of the quantity of raw material mass transferred during the pressure equalization steps. Raw material mass, which was not transferred to a parallel vessel by equalization, leaves the discharge system with the solid polymer product. For economical operation a portion of these fluids must be processed for recovery to the reaction system. The raw material efficiency was effected by the minimum pressure obtained by the steps of vessel pressure equalization. At increasing final pressure of the fourth step, a larger quantity of the valuable raw materials exits with the solid polymer product in streams **14** or **14'**. These fluid materials are lost or must be processed by downstream operations for recovery.

- 20 The "removal ratio" was defined at the mass of raw material removed relative to the mass of solid polymer product. The mass of raw material includes the initial vent through lines **14** or **14'** along with fluid transported with the solid polymer product through lines **14** or **14'**. This "removal ratio" was shown to increase with liquid quantity in the discharge. The cost of recovering or losing valuable raw material increases with liquid quantity in the discharge. In this Example 17 the "removal ratio" increased from 0.1182 to 0.1481 lb fluid per lb of polymer as the liquid concentration in streams **8** or **8'** increased from 15.59 to 29.61 weight percent. A high liquid content in streams **8** and **8'** is clearly undesirable.

-42-

TABLE 6. PROPYLENE HOMOPOLYMER DISCHARGE CYCLE COMPARISON OF LIQUID CONTENT IN DISCHARGE STREAMS 8 AND 8'

Case	1	2	3	4
5 Stream 67 Cooler Outlet				
Liquid (weight %)	24.96	24.96	24.96	24.96
Stream 8 Discharge Fluid Excluding Solids				
10 Vapor Density (lb/ft ³)	3.99	4.05	4.10	4.14
Liquid Density (lb/ft ³)	27.58	27.46	27.34	27.24
Liquid (weight %)	29.61	24.66	19.90	15.59
Profile Vessel Pressure (psia)				
15 10 After Discharge	490.0	490.0	490.0	490.0
10 Equalization with 10'	397.7	388.6	386.8	371.4
12, 12' Before Transfer	20.0	20.0	20.0	20.0
10 After Transfer to 12	299.9	287.9	285.4	265.1
12 Equalization with 12'	206.9	197.3	195.6	178.2
20 12 After Vent, Transfer	20.0	20.0	20.0	20.0
Pressure Equalization Recovered Mass (lb)				
10 Equalize with 10'	77.8	81.6	82.5	88.8
10 Transfer to 12	79.2	78.3	78.7	78.3
25 12 Equalize with 12'	77.7	73.7	73.0	65.7
Stream 14 Vent and Transfer Solid with Fluid to Downstream Processes				
Vessel 12 Vent (lb)	53.4	45.0	43.9	28.0
Solid Product (lb)	968.	968.	968.	968.
30 Fluid with Solid (lb)	90.0	94.2	89.3	86.4
Stream 14 Removal Ratio (Vent+Fluid) / Solid	0.1481	0.1438	0.1376	0.1182
35 Profile Time Duration (seconds)				
10 Discharge and Vent	38.2	38.1	38.0	38.0
10 Equalize with 10'	34.6	35.2	35.3	36.2
10 Transfer to 12	43.8	43.8	43.7	43.7
12 Equalize with 12'	30.2	29.8	29.6	28.5
40 12 Vent and Transfer	59.0	56.5	56.0	50.0
Total Cycle Duration	205.8	203.4	202.6	196.4
Product Discharge (lb/hr)	16,933.	17,133.	17,200.	17,744.

45

Example 18

A fluidized bed polymerization reactor with parallel and interconnected discharge tanks similar to that of **Figure 12** was producing linear low density polyethylene which contained about 10 weight percent polymerized copolymer hexene. The recycle stream 4 at a pressure of 364.7 psia, contained a mixture of hydrogen,

50

nitrogen, methane, ethane, ethylene, hexene and hexane. The pressure at the discharge line **8** and **8'** was 369.0 psia. The pressure was 374.4 psia at the exit of the external cooler **17**. At a temperature below the dew point of 68.7°C there was liquid present in stream **67**, at the exit of the cooler **17**.

5

When operating in “condensed mode”, with the recycle stream **3** containing some liquid, then a portion of the liquid was carried from fluidized bed **2** as the polymer product was intermittently withdrawn through streams **8** and **8'**. For this example, streams **8** and **8'** were located less than 2 feet above the top elevation of the distributor plate **7**. We have found that the relative concentration of liquid to vapor in the discharge streams **8** and **8'** exceeded that in stream **3**. Comparisons are made in **Table 7** with increasing levels of liquid in streams **8** or **8'**, which enters the discharge vessels **10** or **10'**. Discharge conditions and the resulting time duration of the discharge process are displayed in **Table 7**.

15

For the test cases of this Example 18, the two phase fluid recycle stream exiting the cooler **17** was separated into a primary recycle stream **3** and a bypass stream **19**. The bypass stream was returned to the reactor fluidized bed **2**, at an elevation above that of the polymer product discharge streams **8** and **8'**. The separation was conducted such that the liquid content of the bypass stream was enriched and the liquid content of the primary recycle stream was reduced. The test cases with reduced liquid at the reactor inlet, resulted in reduced liquid in the fluid mixture exiting with the solid polymer product in the discharge streams **8** and **8'**.

20

Example 17 includes a more detailed discussion of the discharge process steps, the results of which are summarized in **Table 7** for this Example 18.

25

For the four test cases in this Example 18 the polymer product had a solid phase density of 57.3 lb/ft³. For a given semi-batch discharge cycle, the solid polymer product occupied a volume of 20.02 ft³ in the vessels. Each discharge event

30

removed 1,147 lb of solid polymer product from the reactor fluidized bed **2**. The balance of volume was occupied by raw material fluids. These fluids were in the vapor and optionally liquid phase. They comprised unreacted monomers, comonomers and inert species. The total volume in the interconnecting system for vessels **10** and **10'** was 102% of the available volume for vessels **12** and **12'**.

The total time duration of the discharge process is illustrated in **Table 7**. Cases with multiple venting and equalization steps are included. Time duration for valves to open and close are included in each event. The total time duration includes several sequential batch steps. These were identified in Example 17.

To complete the discharge process, the solid polymer product and some remaining raw material fluids were transferred through either lines **14** or **14'**, to downstream processing equipment. The first vessel equipment into which vent was taken and transfer was completed had an available volume of 6 times the available volume in vessel **10**.

The product removal capacity of the production facility was limited by the time necessary to economically complete a discharge and pressure equalization cycle. When operating in "condensed mode", with the discharge of fluid containing some liquid, the time duration necessary to complete the intermittent discharge process was shown to increase as the quantity of liquid in the discharge streams **8** and **8'** was increased.

In this Example 18 the product removal capacity of the discharge system decreased from 26,118 to 25,954 lb polymer per hour as the liquid concentration in streams **8** or **8'** increased from 4.29 to 16.77 weight percent.

Also included in **Table 7** is a summary of the quantity of raw material mass transferred during the pressure equalization steps. Raw material mass, which was

-45-

not transferred to a parallel vessel by equalization, leaves the discharge process with the solid polymer product. For economical operation a portion of these fluids must be processed for recovery to the reaction system. The raw material efficiency was affected by the minimum pressure obtained by the steps of vessel pressure equalization. At increasing final pressure, a larger quantity of the valuable raw materials exits with the solid polymer product in streams **14** or **14'**. These fluid materials are lost or must be processed by downstream operations for recovery.

The "removal ratio" was shown to increase with liquid quantity in the discharge. In this Example 18 the "removal ratio" increased from 0.0138 to 0.0161 lb fluid per lb of polymer as the liquid concentration in streams **8** or **8'** increased from 4.29 to 16.77 weight percent. High liquid concentrations in streams **8** and **8'** are not desirable.

TABLE 7. POLYETHYLENE HEXENE COPOLYMER DISCHARGE CYCLE
COMPARISON OF LIQUID CONTENT IN DISCHARGE STREAMS **8** AND **8'**

Case	1	2	3	4
Stream 67 Cooler Outlet				
Liquid (weight %)	15.25	15.25	15.25	15.25
Stream 8 Discharge Fluid Excluding Solids				
Vapor Density (lb/ft ³)	1.93	1.86	1.76	1.76
Liquid Density (lb/ft ³)	40.78	40.26	38.66	38.12
Liquid (weight %)	16.77	15.07	7.56	4.29
Profile Vessel Pressure (psia)				
10 After Discharge	364.7	364.7	364.7	364.7
10 Equalization with 10'	249.2	245.6	246.9	245.7
12, 12' Before Transfer	20.0	20.0	20.0	20.0
10 After Transfer to 12	159.2	154.3	155.3	154.1
12 Equalization with 12'	89.2	85.4	84.4	83.8
12 After Final Transfer	20.0	20.0	20.0	20.0
Pressure Equalization Recovered Mass (lb)				
10 Equalize with 10'	36.1	35.0	33.8	33.6
10 Transfer to 12	27.7	26.5	25.7	25.6
12 Equalize with 12'	20.5	19.4	19.1	18.9
Stream 14 Transfer Solid with Fluid to Downstream Processes				
Solid Product (lb)	1,147.	1,147.	1,147.	1,147.
Fluid with Solid (lb)	18.5	17.0	16.0	15.8

-46-

Stream 14 Removal Ratio					
Fluid / Solid		0.0161	0.0148	0.0139	0.0138
Profile Time Duration (seconds)					
5	10 Discharge and Vent	22.1	22.1	22.1	22.1
	10 Equalize with 10'	25.3	24.9	24.8	24.6
	10 Transfer to 12	36.1	36.1	36.0	36.0
	12 Equalize with 12'	14.7	14.6	14.8	14.7
	12 Final Transfer	60.9	60.8	60.8	60.7
10	Total Cycle Duration	159.1	158.5	158.5	158.1
Product Discharge (lb/hr)		25,954.	26,051.	26,051.	26,118.

15 Example 19

A fluidized bed polymerization reactor with parallel and interconnected discharge tanks similar to that of **Figure 12** was producing linear low density polyethylene which contained about 9 weight percent polymerized copolymer butene. The recycle stream **4** at a pressure of 364.7 psia, contained a mixture of hydrogen, nitrogen, methane, ethane, ethylene, butene, butane and isopentane. The isopentane being added to promote partial condensation of the recycle stream. The pressure at the discharge line **8** and **8'** was 369.0 psia. The pressure was 375.2 psia at the exit of the external cooler **17**. At a temperature below the dew point of 65.4°C there was liquid present in stream **67**, at the exit of the cooler **17**.

When operating in “condensed mode”, with the recycle stream **3** containing some liquid, then a portion of the liquid was removed from fluidized bed **2** as the polymer product was intermittently withdrawn through streams **8** and **8'**. For this example, streams **8** and **8'** were located less than 2 feet above the top elevation of the distributor plate **7**. We have found that the relative concentration of liquid to vapor in the discharge streams **8** and **8'** exceeds that in stream **3**. Comparisons are made in **Table 8** with increasing levels of liquid in streams **8** or **8'**, which enters the discharge vessels **10** or **10'**. Discharge conditions and the resulting time duration of the discharge process are displayed in **Table 8**.

-47-

For the test cases of this Example 18, the two phase fluid recycle stream exiting the cooler **17** was separated into a primary recycle stream **3** and a bypass stream **19**. The bypass stream was returned to the reactor fluidized bed **2**, at an elevation above that of the polymer product discharge streams **8** and **8'**. The separation
 5 was conducted such that the liquid content of the bypass stream was enriched and the liquid content of the primary recycle stream was reduced. The test cases with reduced liquid at the reactor inlet, resulted with reduced liquid in the fluid mixture exiting with the solid polymer product in the discharge streams **8** and **8'**.

10 Example 17 includes a more detailed discussion of the discharge process steps, the results of which are summarized in **Table 8** for this Example 19.

For the four test cases in this Example 19 the polymer product had a solid phase density of 57.3 lb/ft³. For a given semi-batch discharge cycle, the solid polymer
 15 product occupied a volume of 20.02 ft³ in the vessels. Each discharge event removed 1,147 lb of solid polymer product from the reactor fluidized bed **2**. The balance of volume was occupied by raw material fluids. These fluids were in the vapor and optionally liquid phase. They comprised unreacted monomers, comonomers and inert species. The total volume in the interconnecting system for
 20 vessels **10** and **10'** was 102% of the available volume for vessels **12** and **12'**.

The total time duration of the discharge process is illustrated in **Table 8**. Cases with multiple venting and equalization steps are included. Time duration for valves to open and close are included in each event. The total time duration
 25 includes several sequential batch steps. These were identified in Example 17.

To complete the discharge process, the solid polymer product and some remaining raw material fluids was transferred through either lines **14** or **14'**, to downstream processing equipment. The first vessel equipment into which vent was taken and

T05020 "E44" 0303

-48-

transfer was completed had an available volume of 6 times the available volume in vessel **10**.

5 The product removal capacity of the production facility was determined by the time necessary to economically complete a discharge and pressure equalization cycle. When operating in “condensed mode”, with the discharge of fluid containing some liquid, the time duration necessary to complete the intermittent discharge process was shown to increase as the quantity of liquid in the discharge streams **8** and **8'** was increased.

10

In this Example 19 the product removal capacity of the discharge system decreased from 25,727 to 25,663 lb polymer per hour as the liquid concentration in streams **8** or **8'** increased from 4.72 to 20.01 weight percent. Conversely, lower concentrations in streams **8** and **8'** resulted in increased product removal capacity even in the condensed mode.

15

Also included in **Table 8** is a summary of the quantity of raw material mass transferred during the pressure equalization steps. Raw material mass, which was not transferred to a parallel vessel by equalization, leaves the discharge process with the solid polymer product. For economical operation a portion of these fluids must be processed for recovery to the reaction system. The raw material efficiency was affected by the minimum pressure obtained by the steps of vessel pressure equalization. At increasing final pressure, a larger quantity of the valuable raw materials would exits with the solid polymer product in streams **14** or **14'**. These fluid materials are lost or must be processed by downstream operations for recovery.

20

25

The “removal ratio” decreased with decreasing liquid quantity in the discharge. The cost of recovering or loosing valuable raw material increases with liquid quantity in the discharge, which in turn is governed by the quantity of liquid

30

T05030" E42260

injected through line **19** rather than line **3**. In this Example 19 the “removal ratio” increased from 0.0195 to 0.0216 lb fluid per lb of polymer as the as the liquid concentration in streams **8** or **8'** increased from 4.72 to 20.01 weight percent.

5

TABLE 8. POLYETHYLENE BUTENE COPOLYMER DISCHARGE
CYCLE COMPARISON OF LIQUID CONTENT IN DISCHARGE STREAMS **8** AND **8'**

10	Case	1	2	3	4
	Stream 67 Cooler Outlet				
	Liquid (weight %)	17.34	17.34	17.34	17.34
15	Stream 8 Discharge Fluid Excluding Solids				
	Vapor Density (lb/ft ³)	2.10	2.12	2.12	2.19
	Liquid Density (lb/ft ³)	34.27	34.09	33.74	33.45
	Liquid (weight %)	20.01	17.14	10.76	4.72
20	Profile Vessel Pressure (psia)				
	10 After Discharge	364.7	364.7	364.7	364.7
	10 Equalization with 10'	263.7	260.7	259.5	253.8
	12, 12' Before Transfer	20.0	20.0	20.0	20.0
	10 After Transfer to 12	176.0	172.6	171.0	165.0
25	12 Equalization with 12'	103.1	100.9	100.3	95.8
	12 After Final Transfer	20.0	20.0	20.0	20.0
	Pressure Equalization Recovered Mass (lb)				
30	10 Equalize with 10'	38.5	38.6	39.2	40.5
	10 Transfer to 12	32.0	31.3	31.5	31.2
	12 Equalize with 12'	24.7	24.0	23.8	22.5
	Stream 14 Transfer Solid with Fluid to Downstream Processes				
35	Solid Product (lb)	1,147.	1,147.	1,147.	1,147.
	Fluid with Solid (lb)	24.8	24.0	23.8	22.4
	Stream 14 Removal Ratio				
	Fluid / Solid	0.0216	0.0209	0.0207	0.0195
40	Profile Time Duration (seconds)				
	10 Discharge and Vent	22.5	22.5	22.4	22.4
	10 Equalize with 10'	26.1	26.0	26.1	26.5
	10 Transfer to 12	36.1	36.1	36.1	36.1
	12 Equalize with 12'	14.9	14.8	14.8	14.4
45	12 Final Transfer	61.3	61.2	61.2	61.1
	Total Cycle Duration	160.9	160.6	160.6	160.5
	Product Discharge (lb/hr)	25,663.	25,711.	25,711.	25,727.

50

FOR RELEASE BY THE DOE